PATENT SPECIFICATION

(11) 1 406 335

(21) Application No. 21326/73 (22) Filed 4 May 1973

(31) Convention Application No. 7 216 921 (32) Filed 4 May 1972 in (19)

(33) France (FR)

(44) Complete Specification published 17 Sept. 1975

(51) INT CL² D01F 8/14

(52) Index at acceptance

B5B 200 35Y 360 401 510 714 720 725

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(54) CRIMPED COMPOSITE POLYESTER FILAMENTS AND COMPOSITE FILAMENT YARNS AND THEIR PRODUCTION

(71) We, RHONE-POULENC-TEXTILE, a French Body Corporate of 5, Avenue Percier, 75008, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to crimped yarns comprising composite filaments formed from two polyesters which possess different shrinkage properties and behave differently during various mechanical and heat treatments carried out after stretching.

Elastic crimped yarns, based on polymers, have been produced by mechanical processes and by other processes such as combining two yarns twisted in opposite directions, or twisting, setting and then untwisting a multifilament yarn (false twist method).

Yarns made of composite filaments produced by extruding, through the same spinneret hole, at least two polymers, which may or may not be of the same nature but which possess different potential shrinkages, are also undergoing considerable development. Such yarns and filaments possess a latent crimp which is capable of developing during subsequent operations. For the sake of brevity yarns made of such composite filaments will hereinafter be termed "composite filament yarns". In the individual filaments the two polymers may be in sheath-core or side-by-side relationship, filaments of the latter type being conveniently referred to as "double-standard filaments".

Polyester yarns which consist of a single polymer and are crimped by processes which are now conventional, such as passage under tension over a heating edge and the false twist method, have never been entirely satisfactory, since the crimp and the elasticity disappear in time as a consequence of the material flowing under the effect of the stresses t which the yarns are subjected during the production of th finished products such as woven fabrics and knitted fabrics, or during the use of these products.

It has already been proposed to produce composite crimped filaments in which one component is a homopolyester and derived from a dicarboxylic acid and a diol, and the other is a copolyester derived from one or more dicarboxylic acids, at least one of which is common to both polymers, and from a diol together with one or more triols. For example, U.S. Patent No. 3,454,460 describes a composite polyester fibre in which one component is a polymethylene glycol terephthalate, and the other is a copolymer of the same polymethylene glycol terephthalate with the terephthalate of another diol or an isophthalate of a polymethylene glycol.

French Patent No. 1,486,035 describes a composite polyester fibre in which one component is polyethylene terephthalate and the other is the same polyethylene terephthalate crosslinked with trimethylolpropane.

British Patent No. 1,075,689 describes a composite yarn which is capable of developing a helicoidal crimp, which is stable to heat and to deformation, and in which the filaments have a laterally asymmetric cross-section, and the component polymers satisfy certain requirements in respect of crystallinity. One component is preferably polyethylene terephthalate, and among various polymers suitable for use as the other is polytetramethylene terephthalate, i.e. polybutylene terephthalate.

Although all these yarns have elasticity properties which are longer lasting than those of yarns crimped by a conventional mechanical method, they are still not completely satisfactory.

It has now been found that two-component double-stranded composite polyester filaments and composite filament yarns (as defined above) in which one component is polyethylene terephthalate and the other is polybutylene terephthalate crosslinked with trimethylolpropane, (that is to say a copolymer of

polybutylene terephthalate and the terephthalate of trimethylolpropane) possess a more permanent crimp and elasticity than do the kn wn yarns referred to above.

Accordingly the present invention consists in such composite filaments and composite filament yarns, and in articles comprising them, and also in their production by extruding the two polymers side by side through the same holes and subsequently stretching the yarn so formed. The polyethylene terephthalate preferably has a viscosity index (as defined below) between 450 and 800, and a melt viscosity between 800 and 2,500 poises at 290° C; the crosslinked polybutylene terephthalate preferably has a viscosity index between 1,000 and 1,500 and a melt viscosity between 3,500 and 5,500 poises at 260° C.

The proportion of trimethylolpropane in the crosslinked polyester is preferably between 0.2 and 0.6 mol %, especially between 0.3 and 0.4 mol %, based on the terephthalic acid. The crosslinking compound is introduced into the polyester during the polycondensation in a known way.

The relative proportions of the two components in the filaments are determined by the relative speeds of the two metering pumps used to forward the respective components, and can vary between 20 and 80%, but most frequently they will be present in about equal proportions. The cohesion between the two polymers is excellent; no discontinuity can be demonstrated by microscopic examination, even using phase contrast and polarised light.

The new composite filaments and composite filament can be used in the manufacture of woven fabrics, knitted fabrics and carpets, but they are particularly valuable in the hosiery trade where they can be used to make articles which have good wearing properties.

The general method of producing composite filament yarns comprising double-stranded filaments is in itself known. In the present case the two polymers, dry, are fused separately, either in melting devices or in extruders, at between 275° and 300° C in the case of polyethylene terephthalate and at between 255° and 265° C in the case of the crosslinked polybutylene terephthalate. They are metered separately by metering pumps which convey them to two-component spinning installations, where they are extruded together through the same capillaries, the walls of which are preferably heated to a temperature between 260° and 285° C.

These capillaries can have a diameter of, for example, between 0.20 and 0.65 mm: they are not restricted in number, so that yarns having very different numbers of constituent filaments can be made. The spinning speed may be, for example, between 300 and 1,700 m/minute; the yarn formed can be cooled by a stream of air.

The initial yarn is then stretched, generally at a ratio between 2 and 4x, using conventional r integrated known processes, for example while passing over a heated pin or a heated roll, at speeds varying from 200 to 3,000 m/minute.

By this means yarn can be obtained which has a helicoidal crimp (which is characteristic of yarns comprising double stranded filaments) which is very uniform and, in contrast to known composite filament polyester yarns, is not lost by flow; the performance of the yarn is good with respect to mechanical operations such as loading and unloading or over-stretching, with or without subsequent heat treatments such as dry or wet setting. It is particularly noteworthy that this crimp is obtained even in the absence of a separate crimp-developing step, such as heating in boiling water.

The characteristics of the crimp can be varied by changing the stretching conditions and also subsequent treatments, such as over-stretching, heat setting treatments with or without tension, and treatment with boiling water in the absence of tension, i.e. while the yarn is free to shrink.

The following Examples illustrate the invention.

In these Examples, the viscosity index (VI) is determined from the solution viscosity, measured at 25° C on a 1% weight/volume solution (1 g. polyester in 1 cc of solvent) of the polymer in *o*-chlorophenol, using the formula

$$VI = \frac{\text{specific viscosity}}{\text{concentration}} \times 1{,}000$$

in which the concentration is expressed in g/100 ml.

The melt viscosity (MV) of the polymer, expressed in poises, is determined on a Davenport extrusion plastometer.

The extensibility is given by the relationship:

$$E\ \% = \frac{L-l}{l} \times 100$$

in which L represents the length of the uncrimped yarn under a tension of 225 mg/dtex and l represents the length of the untensioned crimp yarn.

From the force-elongation diagram established for the range l to L, the half-uncrimping and half-recrimping forces are read as the ordinate corresponding to $\frac{E\ \%}{2}$ on the abscissa.

The crimp frequency is expressed in numbers of half-waves per cm of uncrimped fibre.

The accompanying drawings are graphs in which permanent deformation (residual elongation expressed as a percentage of the initial length of the crimped yarn) is plotted against elongation imposed during elongation-relaxation cycles carried out as follows: The crimped yarn is subjected to deformation (elongation) up to the threshold of extensibility in successive cycles, each followed by a relaxation of the tension allowing the yarn to revert to its crimped configuration. The ratio of the permanent deformation at the close of each cycle to the length at the beginning of the said cycle represents the degree of permanent deformation that is due to that cycle. The rate of elongation is equal to 10% of the initial length of the crimped sample per minute, and the cycles follow one another without an intervening rest period until breakage occurs. The curves of Figures 1 and 2 are subject to experimental errors up to 1%, and such errors are not significant. The curves obtained are referred to in the Examples, and provide a measurement of crimp permanence.

The foregoing measurements are made on yarn which has been conditioned for 24 hours at 22° C. and 65% relative humidity.

EXAMPLE 1.

In an apparatus for spinning yarns of double - stranded filaments, polyethylene terephthalate (VI=770, MV=2,400 at 290° C) is melted at 300° C, and polybutylene terephthalate crosslinked with 0.4 mol % of trimethylolpropane (VI=1,200, MV=4,900 poises at 260° C) is melted at 256° C. The two fused polymers pass through a transfer through a transfer heater at 285° C and then to a spinneret with 32 holes whose capillaries have a diameter of 0.34 mm; the spinning speed is 1,250 m/minute. The resulting yarn is stretched at a ratio of 2.81 × while passing over a roll at 85° C, and then passes over a plate at 170° C and is wound up at 630 m/minute.

Another yarn is produced in the same way from polyethylene terephthalate and non-crosslinked polybutylene terephthalate (i.e. polybutylene terephthalate homopolymer).

The characteristics of these two yarns, before and after treatment in the free state in water which is gradually brought to the boiling point and held there for 5 minutes are given in Table I.

TABLE I

Characteristics	Yarn not treated with boiling water		Yarn treated with boiling water	
	cross-linked	non-cross-linked	cross-linked	non-cross-linked
Gauge . . . . in dtex	79.3	78.3	—	—
Tenacity . . . . ,, g/tex	32.9	32.8	—	—
Elongation . . . . ,, %	9.3	7.3	—	—
1/2-uncrimping force ,, mg/tex	4.03	0	18.9	3.8
1/2-recrimping force . . ,, mg/tex	13.8	0	14.3	3.2
Extensibility . . . . . ,, %	167	0	227.1	56.1
Crimp frequency . . . . ,, 1/2 wave/cm	5.14	2.10	10.04	5.05
Crimp permanence (Figure 1)			curve 1	curve 2

All the measurements given show the marked superiority of the characteristics of the composite filament yarn produced with cross-linked polybutylene terephthalate; in particular, although the treatment with boiling water substantially improves the qualities of the crimp of the yarn f the invention it is nevertheless not necessary, whilst it is absolutely indispensable if any crimp is to be obtained on the yarn produced from non-crosslinked polymer.

The curves shown in the drawings show also that permanent deformations of substantially the same order are obtained, with the limits of experimental error, as the result of applied deformations which are much higher on the yarns made from cross-linked polybutylene terephthalate (227% + elongation

% as opposed to 56% + elongation %).

EXAMPLE 2.

Following the procedure described in Example 1, composite filament yarns of gauge 75 dtex, 32 filaments are produced from polyethylene terephthalate

(VI=770, MV=2,400 at 290° C)

and either polybutylene terephthalate crosslinked with 0.4 mol % of trimethylolpropane (VI=1,200, MV=4,900 at 260° C) or non-crosslinked polybutylene terephthalate (VI=1,105, MV=4,200 poises at 260° C); after being stretched, these two yarns are relaxed at 120° C in moist air, the winding-up speed after relaxation being 300 m/minute in the case of the yarn containing the crosslinked polyester and 200 m/minute in the case of the others. These different speeds are such as result in the same degree of relaxation in the two yarns; the faster winding-up speed used with the yarn of the invention is an important advantage.

Table II gives the various properties of these yarns.

TABLE II

Characteristics	Yarn not treated with boiling water		Yarn treated with boiling water	
	cross-linked	non-cross-linked	cross-linked	non-cross-linked
Gauge . . . . in dtex	80.6	79.4	—	—
Tenacity . . . . ,, g/tex	35.6	31.5	—	—
Elongation . . . . ,, %	15.2	10.8	—	—
1/2-uncrimping force . . ,, mg/tex	10.7	0	21.3	2.95
1/2-recrimping force . . ,, mg/tex	9.6	0	16.8	2.3
Extensibility . . . . ,, %	43.8	0	224.6	52.1
Crimp Frequency . . . . ,, 1/2 wave/cm	9.75	3.55	9.9	3.81
Crimp Permanence (Figure 1)			curve 3	curve 4

All the characteristics of the yarn produced with crosslinked butylene terephthalate are markedly better than those of the non-crosslinked control yarn.

In this case also, although the development treatment with boiling water improves the qualities of the yarn of the invention, it is nevertheless not indispensable.

EXAMPLE 3.

Following the process described in Example 2, both relaxed and unrelaxed composite filament yarns of gauge 165 dtex, 32 filaments are produced. The characteristics of these yarns, after they have been drained (in the case of those given the boiling water treatment), packaged and conditioned for 24 hours at RH 65 and 22° C, are compared with those of a control composite filament yarn of polyethylene terephthalate and non-crosslinked polybutylene terephthalate, with the results shown in Table III and the graph of Figure 2.

All the indicated properties of the composite filament yarn containing the crosslinked polybutylene terephthalate, and particularly the elasticity, the crimp and the crimp permanence, are markedly better than those of the control yarn which contains non-crosslinked polybutylene terephthalate.

Corresponding characteristics of a typical polyester false twist yarn of the same gauge are also given for comparison.

TABLE III

Characteristics	Non-relaxed yarn, not treated with boiling water		Non-relaxed yarn, treated with boiling water		Relaxed yarn, not treated with boiling water		Relaxed yarn, treated with boiling water		False twist yarn	
	cross-linked	non-cross-linked	cross-linked	non-cross-linked	cross-linked	non-cross-linked	cross-linked	non-cross-linked	not treated with boiling water	treated with boiling water
Gauge dtex	178.0	169.0	—	—	184	171	—	—	172	—
Tenacity g/tex	33.3	33.1	—	—	34.2	35.3	—	—	38	—
Elongation %	19.5	13.6	—	—	26.6	20.5	—	—	17.3	—
1/2-uncrimping force mg/tex	6.45	3.5	29.3	8.0	13.9	5.5	32.6	12.1	10.3	63.6
1/2-recrimping force mg/tex	6.3	3.3	19.9	7.75	12	5.3	24.3	9.9	1.62	17.6
Extensibility %	78.0	44.9	26.6	98.0	26.2	23.3	235.6	88.4	23.9	236.1
Crimp Frequency	6.20	3.08	8.68	5.40	5.21	4.32	8.85	6.35	9.46	12.38
Crimp Permanence (Figure 2)			curve 1	curve 2			curve 3	curve 4		

EXAMPLE 4.

Composite filament yarns according to the invention are spun by the process of Example 1, and stretched 3x while passing over a roll at 130° C at a speed of 600 m/minute. The yarn is then set by passing it over a plate at 110° C and also relaxed at 120° C with a winding-up speed of 200 m/minute.

Table IV gives the elasticity characteristics of these yarns at the various production stages, compared with those obtained for a control composite yarn with a non-crosslinked component.

TABLE IV

Characteristics	Yarn before setting		Set Yarn before relaxation		Yarn after relaxation	
	crosslinked	non-crosslinked	crosslinked	non-crosslinked	crosslinked	non-crosslinked
Yarn not treated with boiling water						
1/2-uncrimping force mg/dtex	21.1	10	24.6	7.6	21.5	11.6
1/2-recrimping force mg/dtex	15.1	8.4	17.3	6.2	17	9.3
Extensibility . . . . . . %	323	202	311	199	54.2	53.5
Yarn treated with boiling water						
1/2-uncrimping force mg/dtex	52.9	37.4	54.8	33.6	61.7	49.3
1/2-recrimping force mg/dtex	30.5	21.8	32.1	20	37.7	28.3
Extensibility . . . . . . %	273	247	266	235	236	202

WHAT WE CLAIM IS:—

1. Two-component double-stranded composite polyester filaments and composite filament yarns (as hereinbefore defined) possessing permanent crimp and elasticity, in which one component is polyethylene terephthalate crosslinked with trimethylolpropane.

2. Filaments and yarns according to claim 1 in which the crosslinked polybutylene terephthalate is produced by adding, during the polycondensation, between 0.2 and 0.6 mol % of trimethylolpropane relative to the terephthalic acid.

3. Filaments and yarns according to claim 2, in which the mol proportion of trimethylolpropane is between 0.3 and 0.4%.

4. Filaments and yarns according to any one of claims 1—3, in which the proportion of each comp nent is between 20% and 80% by weight.

5. Filaments and yarns according to claim 4, in which the components are present in approximately equal proportion.

6. Composite filaments and composite filament yarns according to claim 1 substantially as hereinbefore described.

7. Process for the production of filaments and yarns claimed in any one of claims 1—6, which comprises extruding the two components simultaneously side-by-side through the same spinning orifices and subsequently stretching the resulting filament or yarn.

8. Process according to claim 7, in which the polyethylene terephthalate has a melt viscosity between 800 and 2,500 poises at 290° C, and the crosslinked polybutylene terephthalate has a melt viscosity between 3,500 and 5,500 poises at 260° C.

9. Woven fabrics, knitted fabrics, carpets and hosiery comprising a composite filament or composite filament yarn claimed in any one of claims 1—6 or obtained by a process claimed in claim 7 or 8.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa. 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.